

**BEAMLINE X11A****Funding**

Swiss Federal Institute of Technology  
Research Grant

**Publication**

A. Voegelin and R. Kretzschmar, "Formation and Dissolution of Single and Mixed Zn and Ni Precipitates in Soil: Evidence from Column Experiments and Extended X-ray Absorption Fine Structure Spectroscopy," *Environ. Sci. and Tech.*, **39**, 5311-5318 (2005).

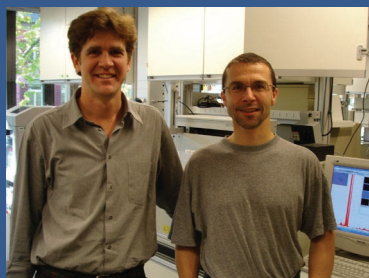
**For More Information**

Andreas Voegelin, Soil Chemistry Group,  
Department of Environmental Sciences,  
Swiss Federal Institute of Technology  
(ETH) Zurich, Switzerland

Email: voegelin@env.ethz.ch

Ruben Kretzschmar, Professor of Soil  
Chemistry, Department of Environmental  
Sciences, Swiss Federal Institute of Technology (ETH) Zurich, Switzerland

Email: kretzschmar@env.ethz.ch



Authors (from left) Ruben Kretzschmar and Andreas Voegelin

## Immobilization Processes in Soils Contaminated with Several Heavy Metals

A. Voegelin and R. Kretzschmar

Department of Environmental Sciences, Swiss Federal Institute of Technology, Zurich, Switzerland

*Contaminated soils are often polluted with a mixture of heavy metals. Little is currently known about the effects of these cocktails on the immobilizing role of heavy-metal precipitates in contaminated soils. For the case of Zn-Ni, we found that more Zn than Ni was retained in a soil leached with heavy-metal containing solutions and that the amounts did not vary whether the metals were present alone or together. Synchrotron spectroscopy showed that Zn and Ni formed individual precipitates when present alone and a single mixed precipitate when present together. This mixed precipitate dissolves much faster than the pure Ni precipitate, indicating a mobilizing effect of Zn on Ni in the case of a combined contamination. Our results demonstrate that the interactions of different metals need to be considered when assessing the relevance of heavy-metal precipitation reactions in contaminated soils.*

Contamination of soils with heavy metals can cause a reduction in crop yield or a contamination of underlying groundwater. The formation of heavy-metal bearing minerals in soils may attenuate those adverse effects and has been therefore extensively studied in recent years. However, soils are often contaminated by several heavy metals and little is still known about the effects to be expected in such cases. We therefore systematically investigated the formation and dissolution of nickel (Ni) and zinc (Zn) precipitates in soil in the presence of only one or both of these metals. Heavy-metal precipitates in soils are weakly crystalline and occur at low concentrations. Synchrotron-based x-ray absorption spectroscopy is a unique method for obtaining direct molecular-scale information on the binding of metals in those systems. Taking advantage of these possibilities, we employed a combined approach of controlled laboratory column studies and extended x-ray absorption fine structure (EXAFS) spectroscopy to investigate the interaction of Ni with Zn in a natural soil.

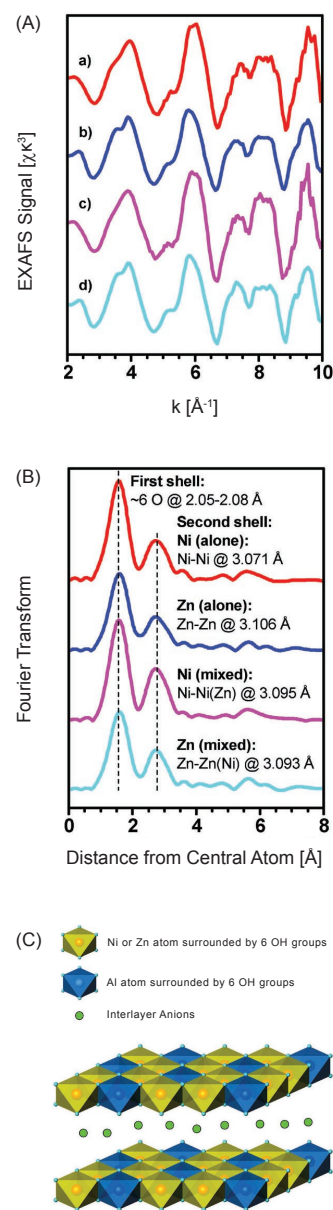
A neutral soil was packed into a chromatographic column and leached over a long period of time with solutions containing low concentrations of Zn and/or Ni that are realistic for actual environmental systems. We found that about twice as much Zn than Ni was retained in the soil when reacted with either Zn or Ni. Interestingly, the same amounts of Zn and Ni were retained in the soil when present together in solution. While this finding might suggest that Zn and Ni acted independently, a different picture was obtained from EXAFS spectroscopy.

**Figure 1** shows (A) EXAFS spectra of the reacted soil samples, (B) their Fourier transforms, and (C) the structure of a layered double hydroxide (LDH) type phase (see also caption). Following a fingerprinting approach, i.e. comparing the experimental spectra (A) to those of known reference minerals, we concluded that Ni and Zn were incorporated into LDH-type minerals in all studied cases. Considering the mixed-metal experiment, the question to be answered by EXAFS spectroscopy was whether Zn and Ni would precipitate into a mixed ZnNi-LDH or form individual precipitates as in the single-metal experiments. We therefore analyzed the Fourier transforms of the EXAFS spectra (see panel B), in which peaks at an increasing distance from the central atom of

interest (Ni or Zn) correspond to different shells of neighboring atoms. While the first peak results from the six oxygens of the hydroxyl groups surrounding Zn or Ni in the octahedra, the second peak results from the next nearest Zn or Ni neighbors in the octahedral sheet (see panel C). For the experiments with either Zn or Ni, we find that the distance between neighboring Zn atoms is significantly larger than between neighboring Ni atoms, due to the larger ionic radius of  $\text{Zn}^{2+}$  than  $\text{Ni}^{2+}$ . In the mixed-metal experiment, we would find the same distance if the metals had precipitated into individual phases. However, the analysis of the Fourier transforms of the mixed-metal sample clearly shows that the distances for Zn and Ni converge. Zn and Ni therefore seem to have precipitated into a single mixed ZnNi-LDH.

Formation of such a mixed NiZn-LDH has a significant impact on the immobilization of Ni or Zn in soil. Leaching the metal-enriched soils with acidified water at pH 3.0, we found that the Zn-LDH dissolved much more rapidly (within minutes) than the Ni-LDH (within days). The mixed NiZn-LDH in the mixed-metal system dissolved almost as fast as the pure Zn-LDH, and considerably faster than the pure Ni-LDH. Thus, the presence of Ni only had a minimal immobilizing effect on Zn, while the presence of Zn in turn led to the incorporation of Ni in a substantially less acid-resistant phase.

Our results show that heavy metals present in mixtures may behave significantly different than if present alone. Further research on this issue is warranted to improve our understanding of heavy metals in contaminated environmental systems. While sorption and extraction studies provide macroscopic information on the interactions of different types of heavy metals in soils, synchrotron-based spectroscopy is required to obtain complementary molecular-scale information on the effective reaction mechanisms.



**Figure 1.** (A) EXAFS spectra of a) Ni in soil reacted with Ni, b) Zn in soil reacted with Zn, c) Ni and d) Zn in soil reacted with Ni and Zn. (B) Fourier transforms of EXAFS spectra shown in the left panel, indicating the position of different atomic shells around the central atom. (C) Structure of layered double hydroxide (LDH), which is composed of divalent (Zn or Ni) and trivalent (Al) cations (double) that are coordinated by six OH groups (hydroxide), forming octahedral sheets in a layered arrangement.